THE JOHNS HOPKINS UNIVERSITY

The Absorption Coefficient of Solutions of Cobalt Chloride in Water and Various Alcohols for Monochromatic Radiation

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY WITH THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

BY

JOHN FOSTER HUTCHINSON

June 4, 1916

EASTON, PA.:
ESCHENBACH PRINTING CO.
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ij6744

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The Absorption Coefficient of Solutions of Cobalt Chloride in Water and Various Alcohols for Monochromatic Radiation[1]

Experiments have shown that in the case of certain solutions the absorption of monochromatic radiation may be represented by the formula

$$I = I_o \times 10^{-\alpha t} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where I_o is the original intensity of the radiation. I is the intensity of the radiation after passing through a layer of solution of thickness t millimeters, and α is a constant for the solution in question called the *absorption coefficient* of the solution for the specified frequency of radiation.

Experiments have also shown that different values of α are obtained if there is any change in:

(*a*) the nature of the solvent or of the dissolved substance,
(*b*) the concentration of the solution,
(*c*) the temperature,
(*d*) the wave-length of the radiation, etc.

To solve the problem of light absorption in solutions it is necessary to determine the explicit form of the relation between the absorption coefficient α, and the quantities of which it is a function. At the present time our knowledge is far too meagre to indicate more than a qualitative idea of the nature of this relation.

In the present investigation α has been measured in those regions of the spectrum where the pure solvents possess appreciable absorption. It is assumed that the total absorption of the solution is the sum of two parts, the first being the absorption due to the presence of the salt, the second being the absorption due to the pure solvent. In calculating this

[1] This is a report on part of an investigation carried out with the aid of a grant from the Carnegie Institution of Washington.

second part, it is assumed that the absorption due to the solvent is the same as it would be if there were no dissolved salt present. We, therefore, write

$$\alpha = Ac + \alpha_o$$

where α_o is the absorption coefficient for the pure solvent, c is the concentration in gram-molecules of salt per liter of solution, and A is called the *molecular absorption coefficient* of the salt in the solution. From this relation we get

$$A = \frac{\alpha - \alpha_o}{c} \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

The present investigation consisted of a systematic and thorough study of the absorption coefficient α. This quantity has been measured at intervals of $20\mu\mu$ to $40\mu\mu$ throughout the region of the spectrum from $600\mu\mu$ to $1300\mu\mu$ for many solutions. The work has been restricted to a study of inorganic salts in aqueous and alcoholic solution. All the measurements have been carried out with solutions at room temperature. The values of α, when plotted as ordinates against the corresponding wave-lengths as abscissas, form the *absorption curve*. For each salt a series of solutions varying in concentration from saturation to moderate dilution were prepared, and the absorption curve has been drawn for each solution. From the measured values of α and α_o, and from the known value of c, A has been calculated for each wave-length by means of formula (2). The values of A for a given wave-length have been plotted as ordinates against the corresponding values of c as abscissas. The curves thus formed will be referred to as the *A-c curves*.

If experiments with any solution show that the relation between α and c is a linear one, and therefore that A in formula (2) is a constant, the A-c curves for such a solution are straight lines parallel to the axis of abscissas. Previous researches[1] [2] have shown that in general the A-c curves are not straight lines parallel to the axis of abscissas, or, in other

[1] Sammlung chemischer und chemisch-technischer Vorträge, **9**, 1 (1904).
[2] Proc. Roy. Soc. Edinburgh, **33**, 156 (1912–13).

words, that A is not a constant.[1] It was the purpose of the present investigation to determine the form of the A-c curves.

The chlorides, nitrates and sulphates of cobalt, nickel, and chromium, and a few other salts, have been studied in this investigation. This paper is a report on the results of the work on a single salt, cobalt chloride.

Apparatus—The apparatus used for determining the light absorption coefficient has been developed by previous workers in this laboratory.[2] The arrangement of the apparatus is shown in Fig. 1. The light from a Nernst glower, g, run at 110 volts on 0.8 ampere direct current from a constant potential storage battery, was rendered parallel by a lens, l_1, 3.8 cm indiameter and with a focal length of 20 cm. The light after passing through cell k' was focussed on the slit A of the spectrograph by a second lens, l_2, 3.8 cm in diameter and with a focal length of 20 cm. A shutter, s, was placed between the glower g and lens l_1, by means of which the light could be turned on and off. The optical system thus far described, consisting of the glower, the two lenses, l_1 and l_2, and the cells, was held by a solid metal frame work, and was perpendicular to the plane of the drawing in Fig. 1. The light after passing through the lens l_2 was reflected on to slit

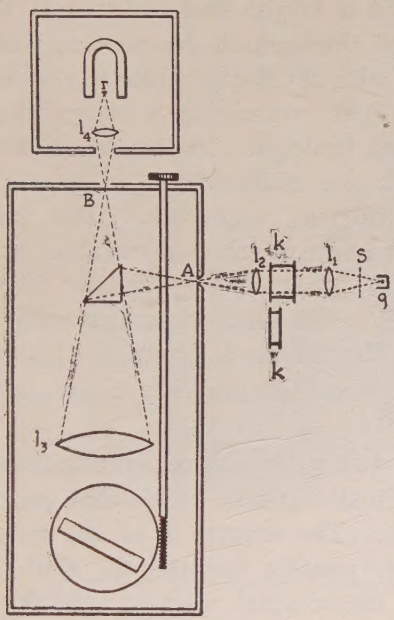

Fig. 1

[1] Beer has stated (Pogg. Ann., **86**, 78–88 (1882)) as a result of his experiments on aqueous solutions of inorganic salts that A is a constant with respect to c. This "law" of Beer has been shown to be the exception rather than the rule, and therefore in this paper no reference has been made to "Beer's Law."

[2] Carnegie Inst. of Wash., Pub. 190 and 230.

A by a right-angle glass prism (not shown in Fig. 1) close to slit A.

The spectrograph consisted of the Littrow mounting of a plane grating. The grating had a ruled area 6 cm by 7.5 cm and was ruled 15000 lines to the inch. The cone of light from slit A was reflected by a right-angle glass prism through the large achromatic lens l_3, 10 cm in diameter and with a focal length of 75 cm. The spectrum was brought to a focus at slit B. The grating possessed a bright first order, and this first order spectrum was used throughout the present work. The dispersion was such that with slit B one millimeter wide a "monochromatic beam" of light containing a wave-length range of 20 A, or $2\mu\mu$, passed through. In this work both slit A and slit B were always one millimeter in width. The correction for finite slit-width was negligible. The grating was mounted on a turn-table which was rotated from the outside by a worm-screw, thus causing various wave-lengths to pass through slit B. The monochromatic beam of light from slit B was focussed by a lens, l_4, 35 cm in diameter and with a focal length of 6 cm on the junction of the radiomicrometer.

The solution for which α was to be determined was placed in two glass cells exactly alike in all respects, except that one cell was thin and the other thick. The energy, I, of the monochromatic beam of light after passing through the thin cell containing a thickness, h, of the solution, and the energy, I′, after passing through the thick cell containing a thickness, h', of solution, were measured in arbitrary units, *i. e.*, deflections of the radiomicrometer. If the initial intensity, I_o, of the light falling on the cell was the same in each case

$$I = I_o \times 10^{-\alpha h}$$

$$I' = I_o \times 10^{-\alpha h'}$$

$$\alpha = \frac{I}{h' - h} \log \frac{I}{I'}$$

$$\text{or } \alpha = \frac{I}{t} \log \frac{d}{d'} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

where d and d' are the deflections produced by I and I′,

respectively, and t is the difference in thickness in millimeters of the two cells. This method eliminated all corrections for reflections from the glass surfaces, and thus gave α directly.

Results

Cobalt Chloride in Water (Figs. 2, 2a)—Twenty-three solutions were prepared varying in concentration from $c = 3.23$ to

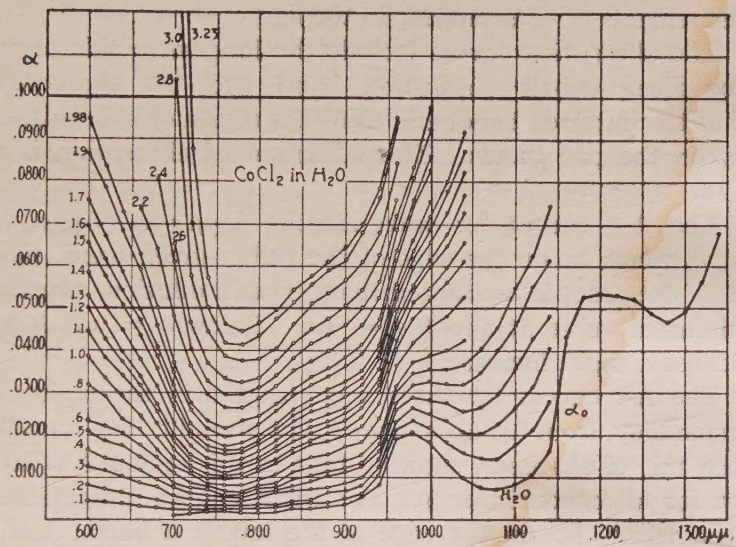

Fig. 2

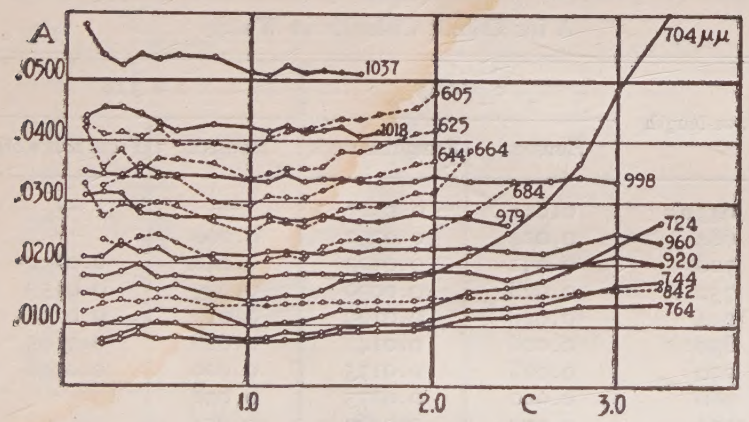

Fig. 2a

$c = 0.1$. The more concentrated solutions were quite stable and showed no signs of decomposition even after standing in the bottles for several days. In the more dilute solutions, however, there appeared a flocculent precipitate which increased their absorption materially. On this account a second set of solutions whose concentrations varied from $c = 1.0$ to $c = 0.1$ were prepared, and the results of the measurements of these appear in the figure.

The absorption curves include the long-wave side of the yellow-green cobalt absorption band and the short-wave side of the infra-red band, and show the region of transmission between the two bands. The minimum of absorption is at $764\mu\mu$.

The A-c curves for wave-lengths $605\mu\mu$ to $764\mu\mu$, inclusive, which lie on the edge of the yellow-green band, show that A decreases in a marked manner with dilution, reaching a minimum value at about $c = 1.0$. Below $c = 1.0$ A experiences a slight increase.

The A-c curves for those wave-lengths in the region of transparency, from $842\mu\mu$ to $979\mu\mu$, are straight lines parallel to the axis of abscissas, showing that in this region A is constant for all concentrations. For wave-lengths greater than $979\mu\mu$, whicb lie on the edge of the infra-red band, A is a

TABLE I

A for Cobalt Chloride in Water

Wave-length	$c = 0.65$		$c = 3.10$	
	Houston	From this work	Houston	From this work
$645\mu\mu$	0.041	0.0340	—	—
684	0.024	0.0232	0.200	—
720	0.031	0.0123	0.041	0.0330
750	0.028	0.0090	0.037	0.0150
794	0.028	0.0109	0.016	0.0138
850	0.028	0.0147	0.018	0.0165
910	0.028	0.0175	0.029	0.0198
980	0.040	0.0275	0.038	—
1070	0.070	0.0762	0.074	—

constant within the error of experiment. The two band edges in question are thus seen to behave quite differently as dilution proceeds. Houston[1] has drawn the absorption curves for two solutions of cobalt chloride in water; and Table I shows the comparison between Houston's values and the values found in this work.

The agreement between Houston's values and the values of A found in the present investigation is far from satisfactory. However, both sets indicate similar changes in A with c.

Cobalt Chloride in Methyl Alcohol. (*Figs. 3, 3a*).

Seven solutions were prepared varying in concentration from $c = 0.7$ to $c = 0.1$. The solutions appeared to keep very well, and no such precipitate was formed as was noticed in the water solutions. The absorption curves show that the character of the absorption of the alcohol solutions was quite different from that of the water solutions, the absorption curve for the alcohol solution being shifted toward the red,

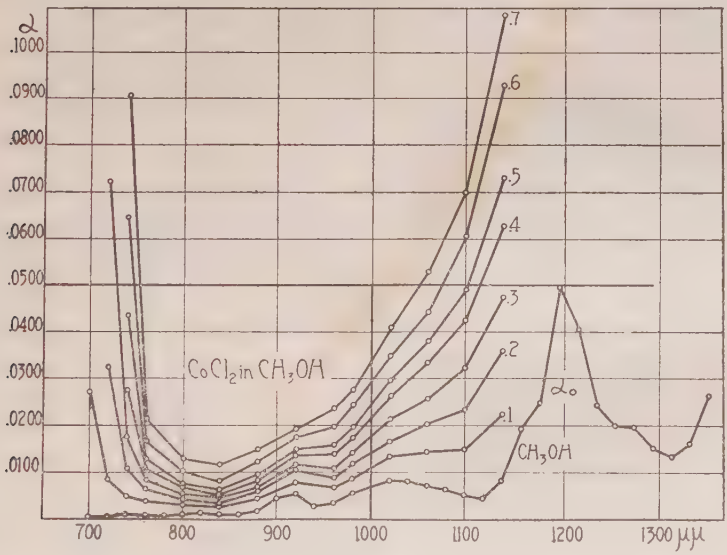

Fig. 3

[1] Proc. Roy. Soc. Edinburgh, **31**, 521 (1910–11).

so that the minimum of absorption was now found at 842 $\mu\mu$, the shift thus amounting to about 80 $\mu\mu$. The shift toward the red of the edge of the band in the green was sufficient to make this band absorb nearly all of the visible red light. (Instead of speaking of the "shift of a band," some have preferred to speak of the bands in the different solvents as entirely different bands.) As a consequence the more concentrated solutions appeared a deeppurple, becoming more and more pink as the dilution increased.

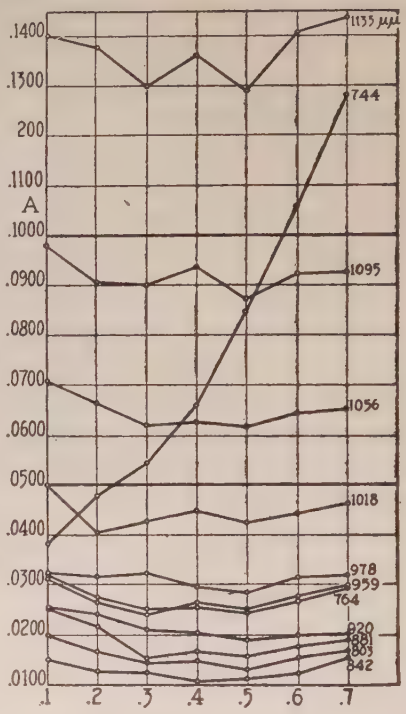

Fig. 3*a*

The A-*c* curve for 744 $\mu\mu$ shows that A decreases by a large amount with dilution, dropping from 0.128 for c = 0.7 to 0.080 for e = 0.1. This is the only A-*c* curve which has been plotted for a wave-length lying on the edge of the red-yellow absorption band, for this edge is tremendously sharp compared to the edge of the analogous band of the water solution. The A-*c* curves for the region of transmission, 764 $\mu\mu$ to 920 $\mu\mu$, and for the edge of the infra-red band 920 $\mu\mu$ to 1134 $\mu\mu$, show that A for these regions of the spectrum remains approximately constant for all concentrations.

Cobalt Chloride in Ethyl Alcohol. (*Fig. 4*)

Four solutions were prepared varying in concentration from c = 0.4 to c = 0.1. A month later a second series of more dilute solutions for which c was 0.08, 0.06, 0.05, 0.04, 0.03, 0.02, 0.01, 0.005, were prepared, and their absorption curves

drawn only in the regions of moderate absorption, from 1056$\mu\mu$ to 1134$\mu\mu$, and for 724$\mu\mu$. In the other regions they either absorbed too much, or too little, so that no confidence could be placed in the values of A.

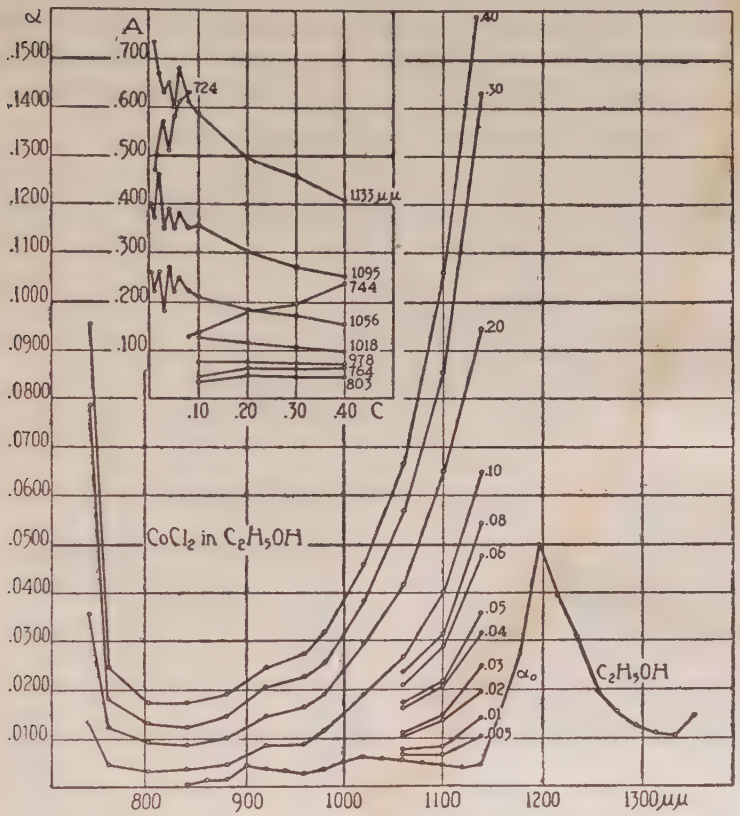

Fig. 4

The absorption curves for the ethyl alcohol solutions are similar in their general character to those for methyl alcohol. The minimum of absorption occurs in the same place, at 842$\mu\mu$, and the steepness of the edge of the bands is much the same. The ethyl alcohol solutions were of a pure deep blue in the higher concentrations, becoming greenish blue as dilution increased.

The A-c curves for $724\mu\mu$ and $744\mu\mu$ show that A decreases with dilution, and the decrease in this case is far greater than in the case of methyl alcohol. For wave-lengths $764\mu\mu$ to $979\mu\mu$ in the region of transmission, A is fairly constant. For the region on the edge of the infra-red band, 1018 to 1134, the A-c curves show that A increases with dilution. These last mentioned curves illustrate the magnitude of the error in the determination of A in the case of very dilute solutions.

Cobalt Chloride in Propyl Alcohol. (*Fig. 5*)

Eight solutions were prepared varying in concentration from $c = 0.434$ to $c = 0.10$. The character of the absorption

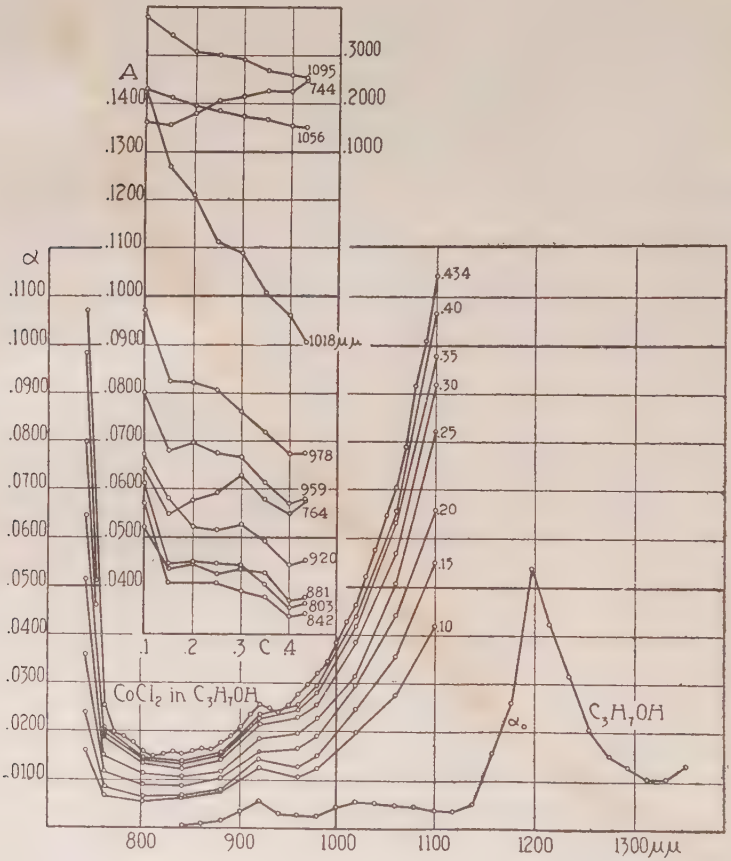

Fig. 5

curves is the same as that of the ethyl alcohol solutions, the minimum of absorption occurring again at $842\mu\mu$, and the steepness of the edges of the bands being similar. The propyl alcohol solutions were also deep blue, becoming a greenish blue upon dilution. The absorption curve for $c = 0.434$ has been drawn in greater detail, readings having been taken at every $10\mu\mu$.

The A-c curve for $744\mu\mu$, lying on the edge of the yellow-red absorption band, shows A to decrease greatly with dilution. This curve (and the A-c curves for $1056\mu\mu$ and $1095\mu\mu$) have been plotted on a scale of ordinates ten times as small as the other A-c curves. For wave-lengths in the region of low absorption, $764\mu\mu$ to $842\mu\mu$, A is approximately constant, although in this region the values of α are so small that the values of A are liable to considerable inaccuracy. The A-c curves for wave-lengths $920\mu\mu$ to $1095\mu\mu$, on the edge of the infra-red band, show that A increases rapidly with dilution.

Cobalt Chloride in Iso-Butyl Alcohol. (*Fig. 6*)

Four solutions were prepared varying in concentration from $c = 0.194$ to $c = 0.05$. The absorption curves have the same character as those for the ethyl alcohol solutions, and the color of the solutions in the bottles was the same, being a deep blue which changed to a greenish blue upon dilution. In preparing the solutions the usual precedure was followed, namely, to make the dilutions by addition of the pure alcohol to the saturated mother solution. It was found that a precipitate appeared immediately upon dilution. The solutions were then filtered, and the concentrations measured by a determination of the density. The value of the concentration determined in this way was found to agree within the error of experiment with the concentration calculated from the known amount of dilution. This showed that the loss by precipitation was either negligible, or that the precipitate contained nearly equal parts of cobalt chloride and iso-butyl alcohol. The filtered solutions appeared quite free from any visible particles.

In the cells they had a somewhat cloudy appearance, suggestive of a colloid condition. They showed slightly a Tyndall cone in blue light. An examination of these freshly filtered iso-butyl alcohol (and also the iso-amyl alcohol) solutions with the ultramicroscope showed that they were not colloidal in nature, but that they contained a number of particles. Whether these particles were newly formed precipitate, or some impurity, is unknown.

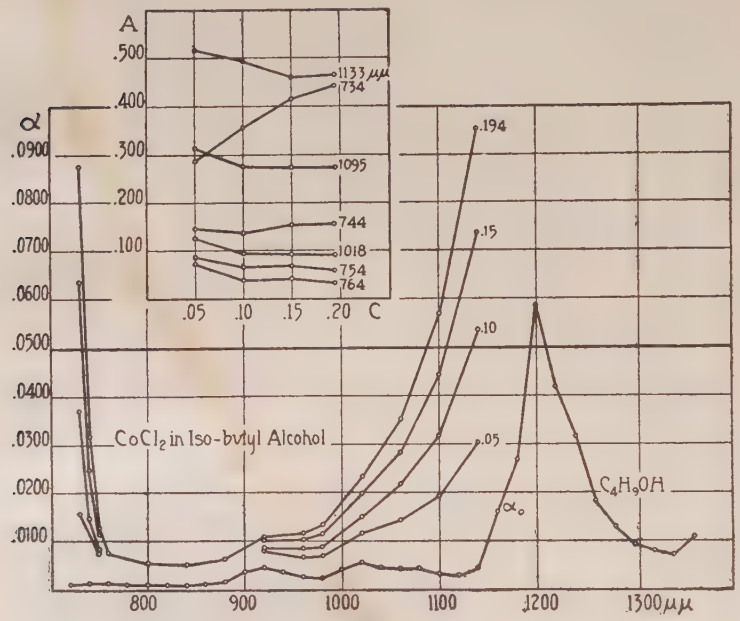

Fig. 6

The A-*c* curves for 734$\mu\mu$ and 744$\mu\mu$, wave-lengths lying on the edge of the yellow-red absorption band, show again that A decreases rapidly with dilution. For the wave-lengths 754$\mu\mu$ and 764$\mu\mu$ in the region of transmission A is a constant. The behavior of the edge of the infra-red band is similar to the case of the propyl alcohol solutions, for A increases with dilution, as shown by the rise in the A-*c* curves for wave-lengths 1018$\mu\mu$ to 1133$\mu\mu$.

Cobalt Chloride in Iso-amyl Alcohol. (*Fig. 7*)

Six solutions were prepared varying in concentration from $c = 0.064$ to $c = 0.010$. The solutions in the bottles were of a deep blue color in the higher concentrations, which changed to a greenish blue upon dilution. The general character of the absorption curves is the same as that of the ethyl alcohol solutions.

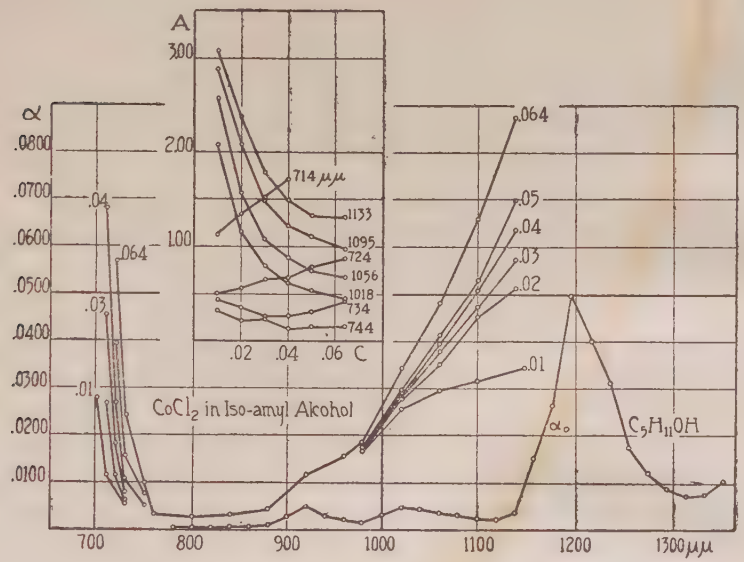

Fig. 7

The iso-amyl alcohol solutions exhibited the same phenomenon of precipitation upon dilution as has been described in the case of the iso-butyl alcohol solutions. They also had the same appearance in the cells, and under the ultramicroscope.

A study was made of the precipitate which was thrown down in these solutions, for the deposit in the case of the iso-amyl alcohol solutions was more abundant than in the case of the deposits in the other cobalt-chloride solutions. The solution was allowed to stand for two weeks, and then the precipitate was filtered off. This precipitate consisted of

blue needle crystals mixed with a flocculent scale-like residue. Analysis showed that in this flocculent residue there was present 54 percent by weight of cobalt chloride. If this precipitate was a compound of the cobalt chloride and the alcohol, this percentage of the chloride would indicate that the compound contained two molecules of the chloride to three of the alcohol.

The A-c curves for the edge of the yellow-red absorption band, at $714\mu\mu$ and $724\mu\mu$, show that A decreases with dilution. In the region of transparency between the two bands A is constant, as shown by the A-c curves for $734\mu\mu$ and $744\mu\mu$. The A-c curves for the edge of the infra-red band show that A increases very rapidly with dilution.

Discussion of Results with Cobalt Chloride

This study of cobalt chloride in water and alcoholic solution brings out the following facts:

In the region of wave-lengths lying on the long wave-length edge of the yellow-red absorption band the A-c curves show that A decreases with dilution. The decrease in A observed in the case of the water solution is considerable, and in the case of the alcoholic solutions this decrease becomes more and more marked as the molecular complexity of the alcohol increases. Jones and Anderson[1] studied solutions of cobalt chloride in water, methyl alcohol, and ethyl alcohol. Plates 2, 4, and 5 of their paper showed that for wave-lengths on the red edge of the yellow-red absorption band A decreased with dilution, and also showed that this decrease was much more marked in the case of the alcoholic solutions than in the water solution. This is in accord with the facts brought out by the measurements discussed in the preceding paragraphs.

In the region of low absorption between the two bands it is concluded that A is constant. As has been mentioned already, in the section concerning cobalt chloride in propyl alcohol, the values of α for the region between the two bands

[1] Carnegie Inst. of Wash., Pub. 110.

are so small that the values of A are in many cases worthless.

In the region of wave-lengths lying on the edge of the infra-red band A experiences deviations from a constant value, and again these deviations show a certain regularity concomitant with the increasing molecular complexity of the solvent. In this region A is nearly constant for the water solutions, but increases with dilution for the alcohol solutions, the increase becoming greater as the molecular weight of the alcohol increases.

Conclusion

The relation between A, the molecular light absorption coefficient of the solution, defined by equation (2), and c, the concentration of the solution in gram-molecules of salt per liter of solution, has been determined. It has been found that in general A is not a constant. In certain cases A decreases with dilution, in other cases A increases with dilution, and in still other cases as dilution proceeds A decreases to a minimum, and then increases again. Another possible combination, namely, that A should increase to a maximum and then decrease, was not met with.

At present there is no adequate theory to explain the facts which have been recorded here. The fact that A varies with c has been probably correctly attributed by Jones and Anderson[1] and others to the formation of complexes, which were considered to be loose chemical compounds of molecules of the salt with molecules of the solvent. Undoubtedly the changes in A with c observed in this investigation may be explained in a qualitative manner by the hypothesis of complexes, or "solvates" as they have been called. But before it can be useful for the interpretation of quantitative data, the solvate hypothesis must be couched in mathematical terms.

The Johns Hopkins University
May 10, 1916

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[1] Loc. cit.

BIOGRAPHICAL NOTE.

John Foster Hutchinson, son of Edwin James Hutchinson, and Jennie (Lilly) Hutchinson, was born in Tonawanda, N. Y., on June 6, 1893. His early training was received in Ferguson, S. C. In 1909 he entered The Military College of South Carolina, and in 1913 was admitted to the degree of Bachelor of Science. In 1914 he received the degree of Master of Arts from the College of Charleston. He entered the Johns Hopkins University in 1914 as a graduate student, making Chemistry the principal subject, Physical Chemistry the first subordinate, and Mineralogy the second subordinate. He attended graduate courses given by Professors Jones, Morse, Reid, Lovelace, Frazer and Swartz. He was the holder of Hopkins Scholarships during the years 1914–1915 and 1915–1916.